

Experiment 8

Qualitative Analysis of Anions

Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook. Be sure to show all work, round answers, and include units on all answers.
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, and Procedure.

Purpose

The purpose of this experiment is to determine what anions are present in an unknown sample. We will be looking for the common anions sulfide (S^{2-}), sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), chloride (Cl^-), bromide (Br^-), iodide (I^-), acetate ($C_2H_3O_2^-$) and nitrate (NO_3^-).

Background

In this lab, you will identify anions in an unknown. Unlike the last lab (Group I Cations), however, you will not just be using a flow chart in which you separate ions away from each other. Instead, in this lab, you first will perform some preliminary tests using $AgNO_3$, $BaCl_2$, and H_2SO_4 . In these tests, certain groups of anions will react while other groups of anions will not react. By analyzing the results of the first part of the experiment, you should be able to eliminate half - if not more- of the anions as possibilities in your unknown. You will then perform confirmatory tests for the remaining anions in question to determine whether the anions are present or absent.

Preliminary Tests

The preliminary tests are described starting on the next page.

Treatment with AgNO_3

The addition of silver nitrate (AgNO_3) to your sample

Some of the anions we are examining will form an insoluble solid (precipitate) with AgNO_3 while other will remain soluble.

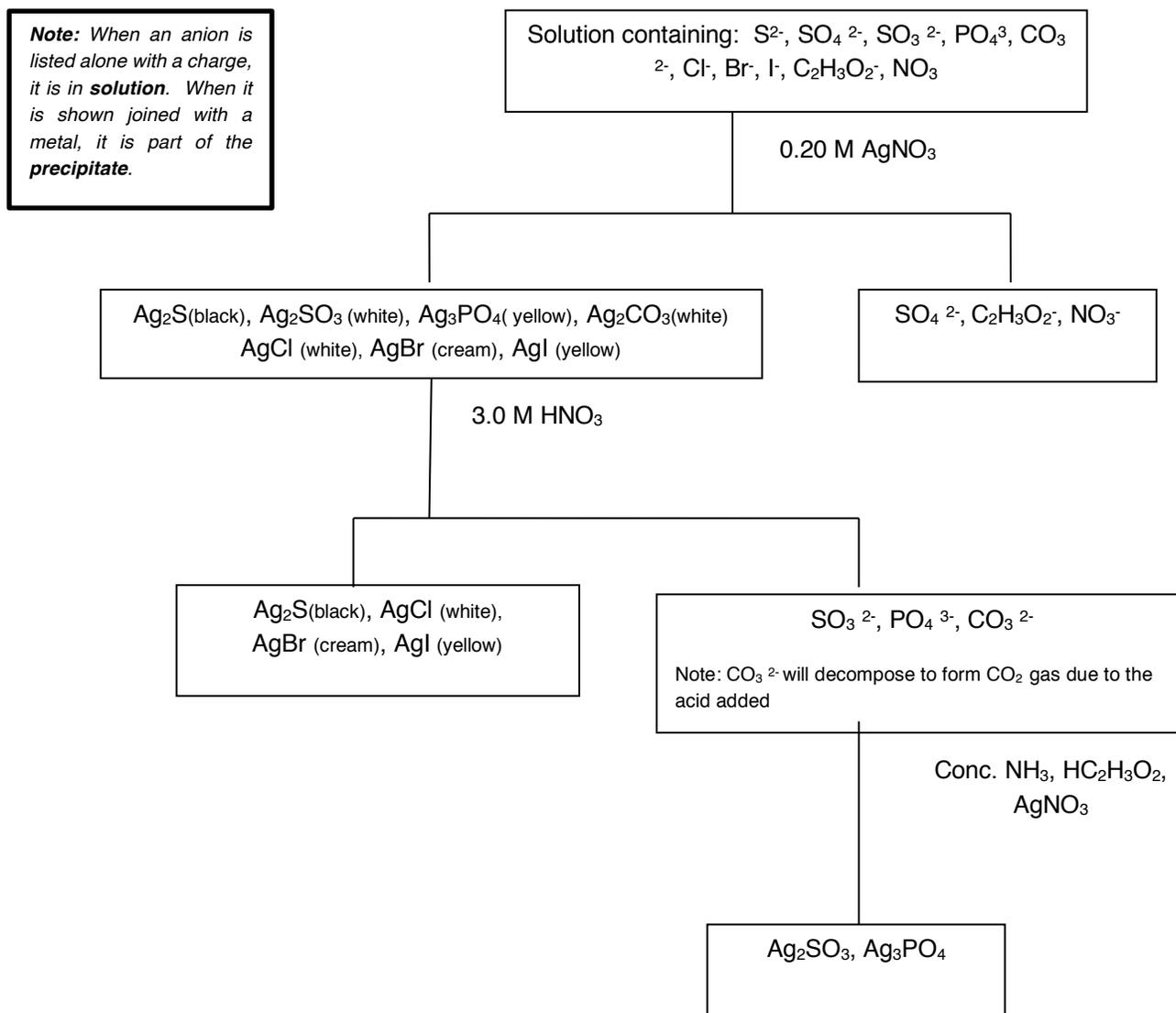
Followed by the addition of nitric acid (HNO_3) to the precipitate

Some of the precipitates formed by the addition of AgNO_3 will dissolve when HNO_3 is added.

Followed by the addition of ammonia (NH_3), then acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), then silver nitrate (AgNO_3) to the supernatant

Some of anions in solution will form a precipitate again.

The results of these steps are summarized in the flow chart below.



In order to understand why certain precipitates form, you should consult the solubility rules and K_{sp} values at the end of this experiment.

Treatment with $BaCl_2$

Starting with a new sample, the second set of preliminary tests involve the addition of barium chloride ($BaCl_2$). Again, some of the anions will form precipitates while others will be soluble.

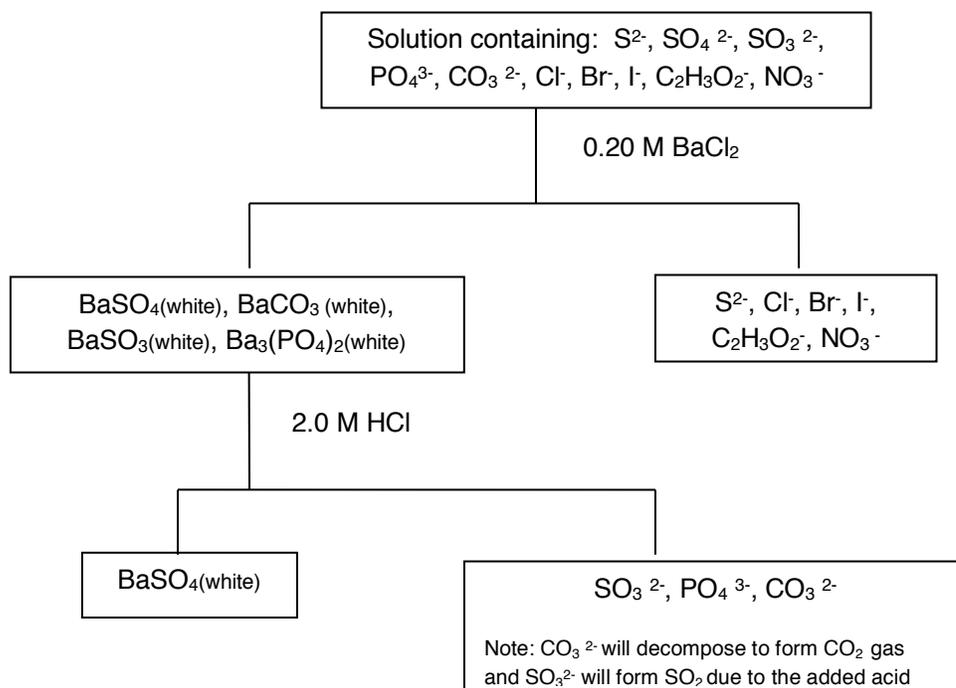
The addition of barium chloride ($BaCl_2$) to your sample

Some of the anions will form a precipitate with $BaCl_2$ while other will be soluble.

Followed by the addition of hydrochloric acid (HCl) to the precipitate

Most of the precipitates formed by the addition of $BaCl_2$ will dissolve when HCl is added. $BaSO_4$ will remain as a solid.

The results of these steps are summarized in the flow chart below.

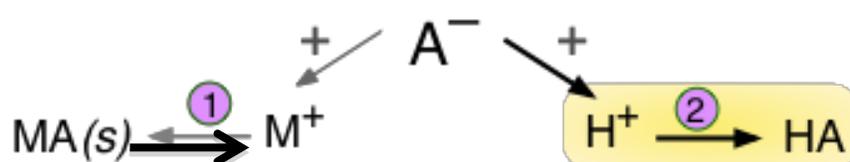


The addition of HCl in the second step fails to dissolve $BaSO_4$ since SO_4^{2-} is the anion of a strong acid.

Other anions also form insoluble precipitates with barium ions such as $BaCO_3$, $BaSO_3$, and $Ba_3(PO_4)_2$. However, these are salts of weak acids and will all dissolve in acidic solution.

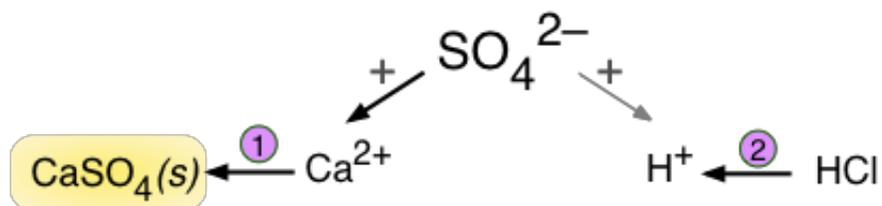
Salts of weak acids are soluble in strong acids

To understand the different behavior of an anion from strong acid or a weak acid, recall La Chatelier's principle and consider a hypothetical salt MA which dissolves to form a cation M^+ and an anion A^- . Assume A^- is from a weak acid HA (more precisely the conjugate base of a weak acid HA). The fact that the acid is weak means that hydrogen ions (always present in aqueous solutions) and M^+ cations will both be competing for the A^- :



The weaker the acid HA, the more reaction (2)'s equilibrium lies to the right. This reaction will use up A^- ions. If an excess of H^+ is made available by the addition of a strong acid, even more A^- ions will be consumed. This will cause reaction (1)'s equilibrium to shift to the right and the solid to dissolve.

On the other hand, strong acids will *not* dissolve salts of strong acids



Consider the addition of a strong acid to a solution containing the salt $CaSO_4$. Recall that the anion of this salt (SO_4^{2-}) is part of the strong acid H_2SO_4 .

In (1), sulfate ions react with calcium ions to form insoluble $CaSO_4$. The addition of a strong acid such as HCl (which will totally dissociate to form H^+ ions (2)) has no effect because H^+ and SO_4^{2-} will not combine into a strong acid H_2SO_4 .

Note: Although H^+ can protonate some SO_4^{2-} ions to form hydrogen sulfate ("bisulfate") HSO_4^- , this amphoteric acid is too weak to reverse (1).

In summary, if the ions are from a weak acid/base, then changing the pH will change the solubility; if the ions are from a strong acid/base, then pH does not change solubility.

Example: Which solid, AgF(s), AgCl(s), AgBr(s), or AgI(s), is more soluble in an acidic solution (as compared to pure water)?

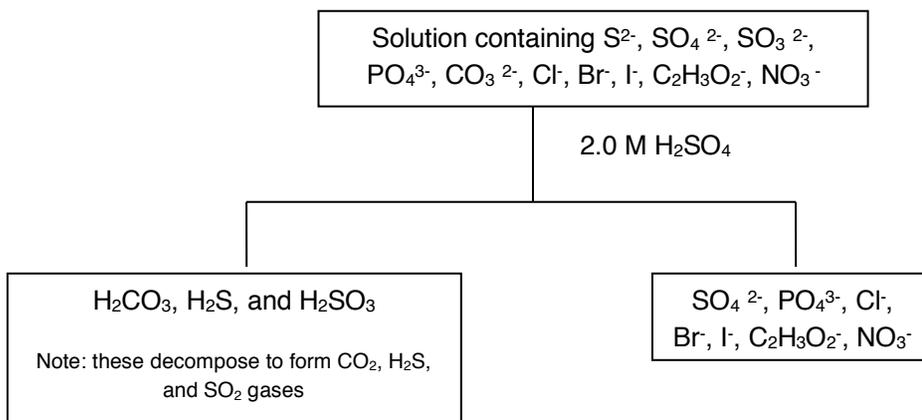
To understand, this write the reaction of H⁺ with AgCl: $\text{AgCl(s)} + \text{H}^{\text{(aq)}} \rightleftharpoons \text{Ag}^{\text{(aq)}} + \text{HCl(aq)}$; since HCl *cannot form* in water because it is a *strong acid* (strong acids dissociate 100% in water), this reaction *does not proceed*;

Repeat with AgF: $\text{AgF(s)} + \text{H}^{\text{(aq)}} \rightleftharpoons \text{Ag}^{\text{(aq)}} + \text{HF(aq)}$; since HF is a *weak acid*, it *can form* in water and the reaction can *proceed*. This means that AgF dissolves more in an acidic solution.

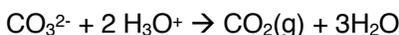
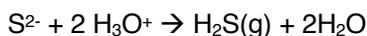
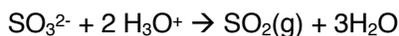
Treatment with H₂SO₄

Starting with a new sample, the third elimination tests involve the addition of 2.0 M sulfuric acid. Some of the anions will react to form a gas while others will undergo no reaction.

The results of these steps are summarized in the flow chart below.



The anions CO₃²⁻, S²⁻, and SO₃²⁻ are the anions of the weak acids H₂CO₃, H₂S, and H₂SO₃ respectively. These weak acids are unstable in solution and decompose to produce the gases CO₂, H₂S, and SO₂ respectively.



If no gases are produced from the acidic solution, then these three anions are absent.

Procedure

Safety

Most of the acids and bases used are very concentrated and can cause chemical burns if spilled. Handle them with care. Wash acid or base spills off of yourself with lots of water. Small spills (a few drops) can be cleaned up with paper towels. Larger acid spills can be neutralized with baking soda, NaHCO_3 , and then safely cleaned up. Neutralize base spills with a vinegar solution (dilute acetic acid).

Solutions containing silver ions cause stains which do not appear immediately. If you suspect that you spilled any of these solutions on yourself, wash off with soap and water.

Wash your hands when finished.

Wear goggles and an apron.

Waste Disposal

Your teacher will provide a waste container for the solutions used in this experiment.

Preliminary Tests

Obtain an unknown from the instructor.

Run the preliminary tests on both the known stock solution (the cations present in solution are listed on the bottle) and your unknown simultaneously for comparison.

Use a fresh unknown sample for each test unless directed otherwise.

Treatment with AgNO_3

Place 10 drops of the solution to be tested (unknown or known) into a small test tube and add 10 drops of 0.2 M AgNO_3 . Stir well to mix. Centrifuge and decant. You may **discard** the supernatant into the waste container.

NO_3^- is a strong oxidizing agent and cannot be in contact with I^- , S^{2-} , and SO_3^{2-} in the known solution since it would oxidize these ions.

Wash the precipitate with several drops of cold deionized water. Centrifuge and discard the washings.

Add 10-15 drops of 3.0 M HNO_3 to the precipitate. Record the color of the precipitate. Centrifuge and **save** the supernatant.

To the supernatant, add concentrated (15 M) NH_3 in the hood until just basic. Then add dilute acetic acid until just acidic. Finally, add 8-10 drops of 0.20 M AgNO_3 . Record your observations.

Dispose of the sample in the waste container.

Treatment with BaCl_2

Place 5 drops of the solution to be tested (unknown or known) into a clean small test tube. Add 5 drops of 0.20 M BaCl_2 . Record your observations. Centrifuge and decant. Discard the supernatant in the waste container.

Add 10 drops of 2.0 M HCl . Stir well and warm. Record your observations. A white precipitate remaining proves the presence of sulfate.

Dispose of the sample in the waste container.

Treatment with H₂SO₄

For this test, test only the unknown.

Place 10 drops of the unknown in a small test tube. In the hood, add 2 drops of 2.0M H₂SO₄. Examine the mixture for evidence of the evolution of gases. If no gases are observed, carefully heat the mixture in the hot water bath. If still no gases are evolved, then CO₃²⁻, S²⁻, and SO₃²⁻ ions are absent. If a gas is evolved, note its odor and color. Below are the properties of some of the gases that are possibly formed:

- CO₂ (carbon dioxide) is colorless and odorless
- H₂S (hydrogen sulfide) is colorless and smells like rotten eggs
- SO₂ (sulfur dioxide) is colorless and smells like burning sulfur

Confirmatory Tests

Before, you begin the confirmatory tests, you will need to analyze the results of the preliminary tests in order to eliminate some of the anions as possibilities. Only run the confirmatory tests on anions that are still in question.

The confirmatory test procedures should be done using both your unknown and a sample known to contain the ion under investigation.

Use a fresh unknown sample for each test unless directed otherwise.

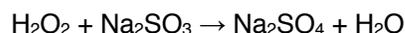
Test for Sulfide Ion, S²⁻ To 1 mL of test solution (known or unknown solution), add 6-8 drops of 6.0 M HCl. Note any odor of H₂S (rotten eggs). Place a strip of moistened lead acetate paper over the mouth of the test tube and heat the test tube in a water bath for several minutes. A darkening of the lead acetate paper as it forms PbS confirms the presence of the S²⁻ ion.

Note: If S²⁻ is found to be present, SO₃²⁻ cannot be present since S²⁻ reduces SO₃²⁻ to S. Therefore the SO₃²⁻ test may be omitted. Note also the modification of the PO₄³⁻ test when S²⁻ is present.

Test for Sulfate Ion, SO₄²⁻ To 2 mL of the test solution (known or unknown solution) add 6.0 M HCl drop by drop until the solution is slightly acidic. If this is a solution containing the unknown, note any gas-formation and carefully check for a sharp odor of SO₂ gas. If an odor is noted, the unknown likely has sulfite ion, SO₃²⁻. Continue with the sulfate test by adding 1 mL of 0.1 M BaCl₂ solution, or more as needed to complete any precipitation. A white precipitate of BaSO₄ proves the presence of SO₄²⁻.

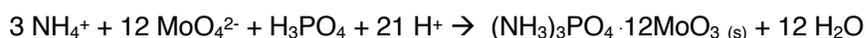
Test for Sulfite Ion, SO₃²⁻ *Continuing with the sample used the sulfate test above...*

Centrifuge the tube from the sulfate ion test to obtain a clear filtrate. Add a drop or two of 0.1 M BaCl₂ to be sure all of the SO₄²⁻ has precipitated. Centrifuge again if more BaSO₄ formed in the solution. Decant the filtrate into a new test tube. To the clear solution, add a few drops of hydrogen peroxide to oxidize any SO₃²⁻ to SO₄²⁻. A white precipitate that forms in the solution proves the presence of SO₄²⁻ as shown in the reaction below:



Test for Phosphate PO₄³⁻ Obtain 10 drops of the sample to be tested (known or unknown). Add 5 drops of 0.5 M (NH₄)₃MoO₄ (ammonium molybdate) and with 5 drops 6.0 M HNO₃. A yellow precipitate of (NH₄)₃PO₄ · 12MoO₃, indicates the presence of phosphate. If a precipitate does not form immediately, heat in a water bath for a few minutes.

The balanced reaction for this test is



Note: If your sample contains sulfide ion (S^{2-}), you must first remove it since it interferes with the phosphate test. To remove the sulfide ion, begin the test by add HCl dropwise to your sample to make it distinctly acidic and heat with stirring for 3 minutes to remove sulfide as H_2S gas. Continue the test by adding the ammonium molybdate and nitric acid as described above.

Test for Carbonate CO_3^{2-} Place a small (pea sized) amount of the solid to be tested into a small test tube. Dip a Nichrome wire loop into $Ba(OH)_2$ solution so that some of the $Ba(OH)_2$ solution adheres to the wire. Place the wire with the suspended $Ba(OH)_2$ just down into the test tube containing the sample to be tested. It should *not* be in contact with the solid.

Add several drops of 2.0 M HCl to the test tube. The rapid evolution of tiny bubbles suggests the presence of carbonate. A cloudy precipitate of $BaCO_3$ formed in the drop of $Ba(OH)_2$ confirms that presence of carbonate.

Note: If SO_3^{2-} is present, it may interfere with the carbonate test as it forms SO_2 gas upon addition of acid and will precipitate with $Ba(OH)_2$ to form $BaSO_3$. To remove SO_3^{2-} , begin the carbonate test by addition an equal amount of sodium peroxide (Na_2O_2) to your solid sample. Then add 5 drops of water, stir, and continue procedure above using the $Ba(OH)_2$ and HCl.

(alternative-OC)

Test for Chloride ion, Cl^- . To a 2 mL portion of the test solution (known or unknown) add a few drops of 6 M HNO_3 as needed to make the solution slightly acidic. If you sample contains sulfide, it must be removed by boiling the solution a moment. The free sulfur formed does not interfere.

Add 1 mL of 0.1 M $AgNO_3$. (Note: If you are testing the unknown and no precipitate forms at this point, the lack of precipitate proves the absence of Cl^- , Br^- and I^-) If a precipitate forms, note the color of the precipitate. $AgCl$ is white, $AgBr$ is cream colored, and AgI is yellow. The color may be a clue to the identity of the anion, but is not always reliable since the colors formed are similar.

Centrifuge the mixture. Test the clear filtrate with 1-2 drops of 0.1 M $AgNO_3$ for complete precipitation. If the filtrate turns cloudy, centrifuge again. Discard the filtrate and keep the precipitate. Wash the precipitate with by adding 10 drops of distilled water to remove excess acid and silver ion. Discard the washings. To the precipitate that remains add 3 mL of distilled water, 4 drops of 6 M NH_4OH , and 0.5 mL of 0.1 M $AgNO_3$. (The proportions are important because we wish to dissolve only the $AgCl$ from any mixture of $AgCl$, $AgBr$, AgI and Ag_2S .) The soluble ions $Ag(NH_3)_2^+$ and Cl^- will form if $AgCl$ is present. These ions will be present in the solution.

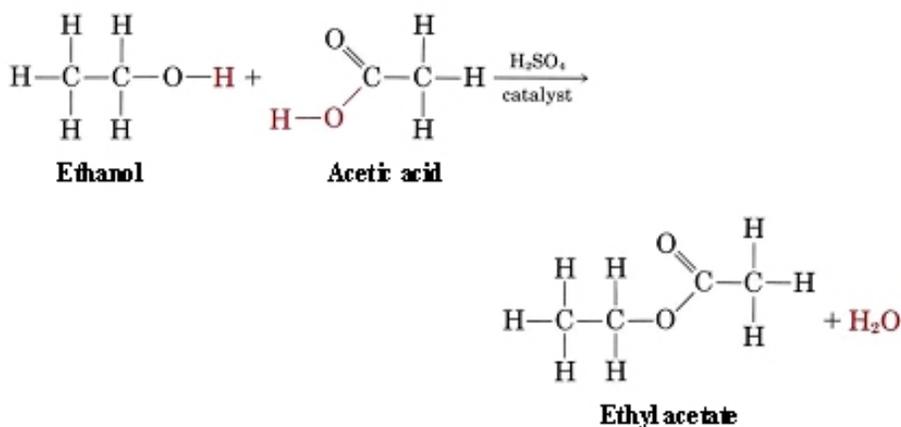
Shake the mixture well and centrifuge. Transfer the clear solution to a clean test tube and acidify with 6 M HNO_3 . A white precipitate of $AgCl$ confirms the presence of Cl^- .

Test for Iodide and Bromide ions, I^- , and Br^- . The complete separation and testing for I^- and Br^- is based upon the selective oxidation of the I^- ion and Br^- ion and their color in cyclohexane. The color of the I_2 (purple) is so dark it will hide the color of Br_2 (brown) if it is also present. Therefore, in order to simplify this experiment, the unknown will **not** contain both Br^- and I^- .

To 2 mL of the test solution, add 6.0 M HCl to make the solution acidic. If you are testing the unknown solution and either S^{2-} or SO_3^{2-} has been found in the unknown, boil the solution to remove the ion. Now add 1 to 2 mL of chlorine water and 2 mL of cyclohexane, stopper the tube, and shake. A purple color indicates I^- is present; a brown (amber) color indicates Br^- is present.

Test for acetate ion, $C_2H_3O_2^-$. Place a small amount of the solid to be tested for acetate ion in a small test tube. Add 3-4 drops of concentrated (18 M) H_2SO_4 and mix thoroughly. Add 4-5 drops of anhydrous ethanol (ethyl alcohol) and mix thoroughly. Heat in a boiling water bath for 1 minute. Carefully smell the

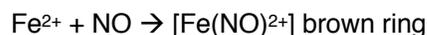
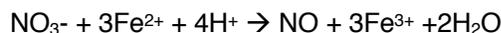
order of the escaping fumes by wafting. A fruity odor of ethyl acetate (similar to juicy fruit gum) escaping proves the presence of acetate ion. Note that if nitrate is present, it forms ethyl nitrate which has a similar order but is somewhat more sweet-smelling.



Test for nitrate ions, NO₃⁻. Iodide and bromide ions (I⁻ and Br⁻) interfere with the nitrate test so they must be removed first if they are present.

If Br⁻ or I⁻ ion is present, treat 10 drops of the test solution with 1 mL of saturated lead acetate PbC₂H₃O₂ solution to precipitate out PbBr₂ or AgI₂. Centrifuge and use the clear supernatant for the nitrate test described below.

If neither Br⁻ nor I⁻ is present, use 10 drops of the test solution directly. Add 5 drops freshly prepared FeSO₄ solution (You must make this solution yourself by dissolving a small amount solid FeSO₄ in 2 mL of deionized water) and mix. Acidify with 3.0 M H₂SO₄, mixing thoroughly. Incline the test tube at a 45° angle and gently pour about 1 mL of concentrated H₂SO₄ (18 M) down the side of the test tube. The concentrated H₂SO₄ will form a layer in the bottom of the tube because of its greater density. Avoid mixing. Let the test tube stand for 3-5 minutes. Look for the presence of a brown ring at the interface of the concentrated H₂SO₄ layer and the test solution layer. The brown ring is Fe(NO)²⁺ and indicates the presence of NO₃⁻. A faint test may be observed more easily by holding the test tube against a white piece of paper. The reaction you have observed occurs in two steps:

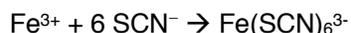


Data Tables

1. For the preliminary tests, record your observations after the addition of each reagent. Be sure to organize your observations including the reagent added, the results for the known and the results for the unknown. Label them clearly.
2. After you have done the preliminary tests, analyze the results and eliminate anions. List the anions you have eliminated in your notebook. Explain your reasoning for eliminating each anion
3. For each confirmatory test, record your observations for both the known and the unknown.
4. Once you identified the anion(s) in your unknown, record the balanced net ionic chemical equations for the reactions involved in each preliminary and confirmatory test for the **unknown sample**.

A Note on Net Reactions

The balanced net reaction describes the chemical changes of any reaction. It is balanced in the usual sense: as many moles of each element in all the reactants as in all the products, and a net charge for all reactants equal to that for all products. It is a net reaction in the sense that only those species in solution that actually change or participate in new bonding situations are included. Consider a test where solid NH_4SCN is added to a solution containing Fe^{3+} . The net reaction, however, does not mention NH_4SCN , since it dissociates in solution to the ammonium ion, NH_4^+ , and the thiocyanate ion, SCN^- . Only the thiocyanate ion is involved in the chemistry; the ammonium ion is a spectator ion. Thus, we write the balanced net reaction as



Writing net reactions thus requires you to be able to identify the reacting species in solution as well as the resultant new product, be it solid precipitate or, as in this case, a complex ion that stays in solution.

Post-Lab Questions

1. Three of the four following compounds listed below will dissolve more in an acidic solution than in water. Which compound will **not** dissolve more in an acidic solution? **Explain.**



2. 0.100g of Na_2CO_3 is added to a 200.0 mL solution of $1.00 \times 10^{-3}\text{M}$ $\text{Ca}(\text{NO}_3)_2$. Will a precipitate form?

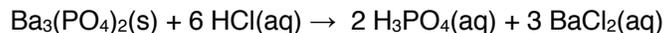
3a. What is the molar solubility (mol/L) of AgCl ?

b. What is the solubility (g/L) of AgCl ?

4. Regarding the first preliminary test, what concentration of AgNO_3 is required to just cause SO_3^{2-} ions to precipitate? Assume the concentration of SO_3^{2-} is 0.10 M.

5. Regarding the second preliminary test, if 100.mL 0.050M BaCl_2 is combined with 150.mL 0.0075M Na_2CO_3 , will a precipitate form?

6. When some precipitates dissolve in HCl or HNO_3 , this is because the hydrogen ion from the strong acid (HCl or HNO_3) reacts with the anion of the precipitate to form a weaker acid. For example, barium phosphate, which is normally insoluble in water, dissolves in HCl because the weaker acid H_3PO_4 (phosphoric acid) is formed.



Write a balanced equation to show how insoluble silver(I) phosphate, Ag_3PO_4 , can dissolve in the strong acid HNO_3 for a similar reason.

Selected Solubility Products and Formation Constants at 25°C

Solubility Rules

Although all compounds have a characteristic solubility in water at a given temperature, some families of compounds are more soluble than others and it is useful to know certain general rules of solubility. We call any substance which has a solubility of less than 0.01 mol/L *insoluble*. If its solubility is greater than 0.1 mol/L, we call it *soluble*. If its solubility is between 0.01 and 0.1 mol/L, we say that it is slightly soluble.

The following solubility rules can be used to determine solubilities in water, with the disclaimer that they are just general guidelines:

1. All sodium, potassium, and ammonium salts are soluble.
2. All nitrates, acetates and perchlorates are soluble.
3. All silver, lead and mercury(I) salts are insoluble.
4. All chlorides, bromides and iodides are soluble.
5. All carbonates, sulfides, oxides and hydroxides are insoluble.
6. All sulfates are soluble except strontium sulfate and barium sulfate.

That having been said, here is a table of solubility product constants.

<u>Compound</u>	<u>Formula</u>	<u>K_{sp}</u>
aluminum hydroxide	Al(OH) ₃	4.6 x 10 ⁻³³
aluminum phosphate	AlPO ₄	6.3 x 10 ⁻¹⁹
barium carbonate	BaCO ₃	5.1 x 10 ⁻⁹
barium chromate	BaCrO ₄	2.2 x 10 ⁻¹⁰
barium fluoride	BaF ₂	1.0 x 10 ⁻⁶
barium hydroxide	Ba(OH) ₂	5 x 10 ⁻³
barium iodate	Ba(IO ₃) ₂	1.5 x 10 ⁻⁹
barium oxalate	BaC ₂ O ₄	2.3 x 10 ⁻⁸
barium sulfate	BaSO ₄	1.1 x 10 ⁻¹⁰
barium sulfite	BaSO ₃	8 x 10 ⁻⁷
barium thiosulfate	BaS ₂ O ₃	1.6 10 ⁻⁵
bismuthyl chloride	BiOCl	1.8 x 10 ⁻³¹
bismuthyl hydroxide	BiOOH	4 x 10 ⁻¹⁰
bismuth(III) sulfide	Bi ₂ S ₃	1 x 10 ⁻⁹⁷
cadmium carbonate	CdCO ₃	5.2 x 10 ⁻¹²

cadmium hydroxide	$\text{Cd}(\text{OH})_2$	2.5×10^{-14}
cadmium iodate	$\text{Cd}(\text{IO}_3)_2$	2.3×10^{-8}
cadmium sulfide	CdS	8.0×10^{-27}
calcium carbonate	CaCO_3	3.8×10^{-9}
calcium chromate	CaCrO_4	7.1×10^{-4}
calcium fluoride	CaF_2	5.3×10^{-9}
calcium hydroxide	$\text{Ca}(\text{OH})_2$	5.5×10^{-6}
calcium iodate	$\text{Ca}(\text{IO}_3)_2$	7.1×10^{-7}
calcium oxalate hydrate	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	1.96×10^{-8}
calcium hydrogen phosphate	CaHPO_4	1×10^{-7}
calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	1×10^{-26}
calcium sulfate	CaSO_4	9.1×10^{-6}
calcium sulfite	CaSO_3	6.8×10^{-8}
chromium(II) hydroxide	$\text{Cr}(\text{OH})_2$	2×10^{-16}
chromium(III) hydroxide	$\text{Cr}(\text{OH})_3$	6.3×10^{-31}
cobalt(II) carbonate	CoCO_3	1.4×10^{-13}
cobalt(III) hydroxide	$\text{Co}(\text{OH})_3$	1.6×10^{-44}
cobalt(II) sulfide	CoS	4.0×10^{-21}
copper(I) chloride	CuCl	1.2×10^{-6}
copper(I) cyanide	CuCN	3.2×10^{-20}
copper(I) iodide	CuI	1.1×10^{-12}
copper(I) sulfide	Cu_2S	2.5×10^{-48}
copper(II) arsenate	$\text{Cu}_3(\text{AsO}_4)_2$	7.6×10^{-36}
copper(II) carbonate	CuCO_3	1.4×10^{-10}
copper(II) chromate	CuCrO_4	3.6×10^{-6}
copper(II) ferrocyanide	$\text{Cu}_2[\text{Fe}(\text{CN})_6]$	1.3×10^{-16}
copper(II) hydroxide	$\text{Cu}(\text{OH})_2$	2.2×10^{-20}
copper(II) sulfide	CuS	6×10^{-37}

copper(II) thiocyanate	$\text{Cu}(\text{SCN})_2$	4.0×10^{-14}
fluorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	1.0×10^{-60}
hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	1.0×10^{-36}
iron(II) carbonate	FeCO_3	3.2×10^{-11}
iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	8.0×10^{-16}
iron(II) sulfide	FeS	6×10^{-19}
iron(III) arsenate	FeAsO_4	5.7×10^{-21}
iron(III) ferrocyanide	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	3.3×10^{-41}
iron(III) hydroxide	$\text{Fe}(\text{OH})_3$	4×10^{-38}
iron(III) phosphate	FePO_4	1.3×10^{-22}
lead(II) arsenate	$\text{Pb}_3(\text{AsO}_4)_2$	4.0×10^{-36}
lead(II) azide	$\text{Pb}(\text{N}_3)_2$	2.5×10^{-9}
lead(II) bromate	$\text{Pb}(\text{BrO}_3)_2$	7.9×10^{-6}
lead(II) bromide	PbBr_2	4.0×10^{-5}
lead(II) carbonate	PbCO_3	7.4×10^{-14}
lead(II) chloride	PbCl_2	1.6×10^{-5}
lead(II) chromate	PbCrO_4	2.8×10^{-13}
lead(II) fluoride	PbF_2	2.7×10^{-8}
lead(II) hydroxide	$\text{Pb}(\text{OH})_2$	1.2×10^{-5}
lead(II) iodate	$\text{Pb}(\text{IO}_3)_2$	2.6×10^{-13}
lead(II) iodide	PbI_2	7.1×10^{-9}
lead(II) sulfate	PbSO_4	1.6×10^{-8}
lead(II) sulfide	PbS	3×10^{-29}
lithium carbonate	Li_2CO_3	2.5×10^{-2}
lithium fluoride	LiF	3.8×10^{-3}
lithium phosphate	Li_3PO_4	3.2×10^{-9}
magnesium ammonium phosphate	MgNH_4PO_4	2.5×10^{-13}

magnesium arsenate	$\text{Mg}_3(\text{AsO}_4)_2$	2.1×10^{-20}
magnesium carbonate	MgCO_3	3.5×10^{-8}
magnesium fluoride	MgF_2	3.7×10^{-8}
magnesium hydroxide	$\text{Mg}(\text{OH})_2$	1.8×10^{-11}
magnesium oxalate	MgC_2O_4	7×10^{-7}
magnesium phosphate	$\text{Mg}_3(\text{PO}_4)_2$	1×10^{-25}
manganese(II) carbonate	MnCO_3	1.8×10^{-11}
manganese(II) hydroxide	$\text{Mn}(\text{OH})_2$	1.9×10^{-9}
manganese(II) sulfide	MnS	2.5×10^{-13}
mercury(I) bromide	Hg_2Br_2	5.6×10^{-23}
mercury(I) chloride	Hg_2Cl_2	5.0×10^{-13}
mercury(I) chromate	Hg_2CrO_4	2.0×10^{-9}
mercury(I) cyanide	$\text{Hg}_2(\text{CN})_2$	5×10^{-40}
mercury(I) iodide	HgI_2	4.5×10^{-29}
mercury(I) sulfate	Hg_2SO_4	7.4×10^{-7}
mercury(I) sulfide	Hg_2S	1.0×10^{-47}
mercury(I) thiocyanate	$\text{Hg}_2(\text{SCN})_2$	3.0×10^{-20}
mercury(II) sulfide	HgS	1.6×10^{-52}
mercury(II) thiocyanate	$\text{Hg}(\text{SCN})_2$	2.8×10^{-20}
nickel(II) carbonate	NiCO_3	6.6×10^{-9}
nickel(II) hydroxide	$\text{Ni}(\text{OH})_2$	2.0×10^{-15}
nickel(II) sulfide	NiS	3×10^{-19}
scandium fluoride	ScF_3	4.2×10^{-18}
scandium hydroxide	$\text{Sc}(\text{OH})_3$	4.2×10^{-18}
silver arsenate	Ag_3AsO_4	1.0×10^{-22}
silver acetate	$\text{AgC}_2\text{H}_3\text{O}_2$	2.0×10^{-3}
silver azide	Ag_3N_3	2.0×10^{-8}
silver benzoate	$\text{AgC}_7\text{H}_5\text{O}_2$	2.5×10^{-5}

silver bromate	AgBrO ₃	5.5 x 10 ⁻⁵
silver bromide	AgBr	5.3 x 10 ⁻¹³
silver carbonate	Ag ₂ CO ₃	8.1 x 10 ⁻¹²
silver chloride	AgCl	1.8 x 10 ⁻¹⁰
silver chromate	Ag ₂ CrO ₄	1.1 x 10 ⁻¹²
silver cyanide	AgCN	1.2 x 10 ⁻¹⁶
silver iodate	AgIO ₃	3.0 x 10 ⁻⁸
silver iodide	AgI	8.3 x 10 ⁻¹⁷
silver nitrite	AgNO ₂	6.0 x 10 ⁻⁴
silver oxalate	Ag ₂ C ₂ O ₄	3.6 x 10 ⁻¹¹
silver sulfate	Ag ₂ SO ₄	1.4 x 10 ⁻⁵
silver sulfide	Ag ₂ S	6 x 10 ⁻⁵¹
silver sulfite	Ag ₂ SO ₃	1.5 x 10 ⁻¹⁴
silver thiocyanate	AgSCN	1.0 x 10 ⁻¹²
strontium carbonate	SrCO ₃	1.1 x 10 ⁻¹⁰
strontium chromate	SrCrO ₄	2.2 x 10 ⁻⁵
strontium fluoride	SrF ₂	2.5 x 10 ⁻⁹
strontium oxalate	SrC ₂ O ₄	4 x 10 ⁻⁷
strontium sulfate	SrSO ₄	3.2 x 10 ⁻⁷
strontium sulfite	SrSO ₃	4 x 10 ⁻⁸
thallium(I) bromate	TlBrO ₃	1.7 x 10 ⁻⁴
thallium(I) bromide	TlBr	3.4 x 10 ⁻⁶
thallium(I) chloride	TlCl	1.7 x 10 ⁻⁴
thallium(I) chromate	Tl ₂ CrO ₄	9.8 x 10 ⁻¹⁵
thallium(I) iodate	TlIO ₃	3.1 x 10 ⁻⁶
thallium(I) iodide	TlI	6.5 x 10 ⁻⁸
thallium(I) sulfide	Tl ₂ S	6 x 10 ⁻²²
thallium(I) thiocyanate	TlSCN	1.6 x 10 ⁻⁴

thallium(III) hydroxide	$Tl(OH)_3$	6.3×10^{-46}
tin(II) hydroxide	$Sn(OH)_2$	1.4×10^{-28}
tin(II) sulfide	SnS	1×10^{-26}
zinc carbonate	$ZnCO_3$	1.4×10^{-11}
zinc cyanide	$Zn(CN)_2$	3×10^{-16}
zinc hydroxide	$Zn(OH)_2$	1.2×10^{-17}
zinc iodate	$Zn(IO_3)_2$	3.9×10^{-6}
zinc oxalate	ZnC_2O_4	2.7×10^{-8}
zinc phosphate	$Zn_3(PO_4)_2$	9.0×10^{-33}
zinc sulfide	ZnS	2×10^{-25}
<u>Formation Constants of Selected Complex Ions, at 25°C</u>	<u>Formula</u>	<u>K_f</u>
	$Ag(CN)_2^-$	5.6×10^{18}
	$Ag(NH_3)_2^+$	1.7×10^7
	$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}
	$Co(SCN)^+$	100
	$Cu(CN)_2^-$	1.0×10^{16}
	$Cu(NH_3)_4^{2+}$	1.0×10^{13}
	$Fe(SCN)^{2+}$	900
	HgI_4^{2-}	4.2×10^{27}
	$Zn(NH_3)_4^{2+}$	2.9×10^9
	$Zn(OH)_4^{2-}$	4.6×10^{17}

Pre-Lab Questions

1. The procedure for chloride analysis makes use of the fact that AgCl can be more easily dissolved than AgBr or AgI in water. Look up the solubility products constants of AgCl, AgBr and AgI and show how their relative solubilities agree with this fact.

2. Write the balanced, net ionic equation for the reaction occurring when:

(a) Ba^{2+} is added to a SO_4^{2-} containing solution

(b) Ba^{2+} is added to a PO_4^{3-} containing solution.

3. Write the balanced, net ionic equation for the reaction occurring when:

(a) Ag^+ is added to a Cl^- containing solution

(b) Ag^+ is added to a PO_4^{3-} containing solution.

4. Why does the known stock solution contain all the anions under investigation except NO_3^- ? Why is the NO_3^- left out?

5. Consider the first step of the second preliminary test-the addition of BaCl_2 to an unknown solution. You may wish to refer to the flow chart on page 144.

a. If you see **no** precipitate form, what anions can you conclude are not in your unknown?

b. If you see a precipitate form, what anions can you conclude are not in your unknown? Be careful!

6. Consider the first two steps of the first preliminary test-the addition of AgNO_3 followed by addition of HNO_3 . If you see a precipitate form with the addition of AgNO_3 and the precipitate dissolves when HNO_3 is added,

a. What anions can you conclude are not in your unknown?

b. List the anions of which one **must** be in your unknown. (Hint: There are three of them.)